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(71)Applicant : DAIHATSU MOTOR CO LTD

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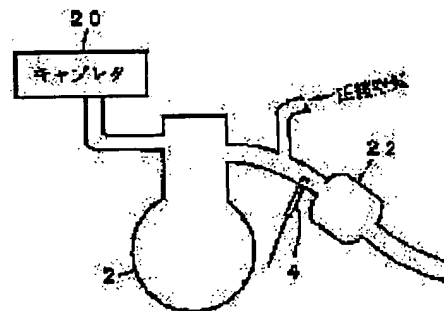
(72)Inventor : TANAKA HIROHISA

(54) DEVICE FOR PURIFYING AUTOMOBILE EXHAUST GAS

(57)Abstract:

PURPOSE: To remove three components in the exhaust gas without performing A/F feed back control.

CONSTITUTION: An engine 2 is provided with an carburetor 20 and a fuel adjusted in A/F is fed to it. A catalyst 22 is provided in an exhaust port of the engine 2 at a position under the engine 2. The A/F feed back control is not performed by a signal of an oxygen sensor. The catalyst on which noble metal such as Pd is deposited on perovskite type complex oxide as the catalyst 22 or it is introduced into a lattice of a perovskite type complex oxide crystal, is used as the catalyst 22.



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JAPANESE

[JP,08-224446,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

Claim(s)]

Claim 1] The automobile exhaust purge which is the engine equipped with the carburetor or the short form fuel injection equipment, is an exhaust gas purge used for the engine which does not perform feed back control of air-fuel ratio by the signal of the oxygen sensor of an engine exhaust port, and is characterized by preparing the catalyst which supported noble metals to the perovskite mold multiple oxide, or was incorporated in the perovskite mold multiple oxide crystal lattice as a catalyst for emission gas purification in an engine exhaust port.

[Claim 2] The location in which the catalyst is prepared is an automobile exhaust purge according to claim 1 which it is directly under an engine.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the automobile exhaust purge excellent in the clarification capacity of a carbon monoxide (CO), a hydrocarbon (THC), and nitrogen oxide (NOx).

[0002]

[Description of the Prior Art] As a three way component catalyst for emission gas purification, the precious metal catalyst which supported noble metals, such as Pt, Rh, and Pd, is put in practical use by alumina support, and it is widely used for it. To be shown in drawing 1, an automobile exhaust purge forms an oxygen sensor 4 in the exhaust port of an engine 2, detects the oxygen density of exhaust gas, calculates A/F (air-fuel ratio) by computer (ECU) 6 based on the detecting signal, and it is controlling the electronic formula fuel injection equipment (EFI) 8 which injects a fuel in an engine 2 so that A/F goes into the predetermined range.

[0003] after performing the durability test of 60 hours to drawing 2 and drawing 3 at 950 degrees C among the engine exhaust gas set as theoretical air fuel ratio (A/F=14.6) in the sample, the activity of the various catalysts which measured the sample on SV(space velocity) = 70000-/o'clock of conditions with **** omission and a model gas testing machine in test piece size (the diameter of 30mm and height are 25mm — cylindrical) is shown. (A) The chart on the left of each drawing of — (C) shows the rate of clarification to the temperature in theoretical air fuel ratio, and right-hand side drawing shows the rate of clarification to A/F when setting the gas temperature included in a catalyst as 400 degrees C, and measuring it. The catalyst (example 3) which supported Pd to the perovskite mold multiple oxide which is one example which explains (A) of each drawing later, and (B) adjust the conventional catalyst (the example b of a comparison) which supported Pd to the alumina, and (C) to the conventional catalyst (the example a of a comparison) and this conventional specification which supported Pt and Rh to the alumina.

[0004] Drawing 2 is the case where fluctuation by each A/F is **0.5 A/F, and the range of A/F (60% window) where each rate of clarification of CO, THC, and NOx can secure 60% or more exists also in the conventional catalyst of (B) and (C). on the other hand — drawing 3 — every — it is the case where fluctuation by A/F is **2.0 A/F, and is shown in (B) and (C) — as — the catalyst of ***** — every — if fluctuation by A/F becomes large also at **2.0 A/F, the rate of clarification of CO will fall and 60% window which can purify three components 60% or more simultaneously will be lost. Therefore, he is trying for the conventional purge to come by performing A/F feedback control as shown in drawing 1 in 60% window where fluctuation of A/F does not exceed **0.5, and A/F is shown by drawing 2 (B) and (C).

[0005] Moreover, directly under an engine, as for the exhaust gas from an engine, A/F is sharply changed by the engine cycle. Therefore, in order to suppress A/F fluctuation in the location of a catalyst like before, a catalyst must be installed in the location detached distantly [engine] so that the A/F fluctuation for every engine cylinder can be eased, and it is attached in the car body lower part generally called an under floor. On the other hand, lowering of exhaust gas temperature reduces catalytic activity. for example, every — the case where fluctuation by A/F is **0.5 A/F — 200 degrees C or less — almost — catalytic activity — being lost — every — when fluctuation by A/F becomes large also at **2.0 A/F, it is 350-400 degrees C or less, and stops already showing catalytic activity with the conventional catalyst, as shown in the chart on the left of drawing 3 (B) and (C) Since it will get cold by the time the exhaust gas from an engine reaches a catalyst if it installs in the location which detached the catalyst distantly [engine], on the conditions that exhaust gas temperature, such as the time of engine start up, is low, a catalyst serves as inactive and the problem by which exhaust gas is not purified arises. Therefore, the cure of using the exhaust pipe from an engine to a catalyst as a double pipe, and keeping it warm is also taken.

[0006] Utilization is expected as a cheap three way component catalyst for emission gas purification with which the catalyst which made noble metals live together as a catalyst in the perovskite mold multiple oxide which consists of a rare earth metal, an alkaline earth metal, and transition metals purifies CO, HC, and NOx (refer to JP,59-87046,A, JP,60-82138,A, and JP,1-168343,A). The exhaust gas purge equipped with A/F feedback control as the exhaust gas purge which this catalyst is used instead of the conventional catalyst which made the alumina support noble metals, and uses this catalyst indicated to be to drawing 1 is planned.

[0007]

[Problem(s) to be Solved by the Invention] If A/F feedback control as shown in drawing 1 is performed, an oxygen sensor and expensive components, such as ECU and EFI, will be needed, and it will become cost high so much. Moreover, since it will get cold by the time the exhaust gas from an engine reaches a catalyst if it installs in the location which detached the catalyst distantly [engine] in order to operate a catalyst also especially at the time of engine start up, when not enough, the cure of heating a catalyst is also still needed [use the exhaust pipe from an engine to a catalyst as a double pipe, and it is made to keep it warm, or]. Even if this invention does not perform A/F feedback control using an oxygen sensor and expensive components, such as ECU and EFI, it also aims using a carburetor (carburetor) and a short form fuel injection equipment at offering the purge with which exhaust gas is purified.

[0008]

[Means for Solving the Problem] The exhaust gas purge of this invention is applied to the engine which does not perform feed back

control of air-fuel ratio by the signal of the oxygen sensor of an engine exhaust port. And the catalyst which supported noble metals to the perovskite mold multiple oxide, or was incorporated in the perovskite mold multiple oxide crystal lattice as a catalyst for emission purification is used. Since it is stopped that directly under [engine], then exhaust gas are cooled in the location in which the catalyst is prepared, a means to keep exhaust gas warm, and a means to heat a catalyst become unnecessary, a catalyst works from immediately after putting an engine into operation between the colds, and it is advantageous for emission gas purification.

[0009] The catalyst used by this invention is $\text{BO}(\text{A}1-x\text{A}'x)_3$ (among a formula at least one sort of A of La, Nd, and the Pr). A' At least one sort in Ce, Mg, calcium, Sr, Ba, and Y, B — Co, Mn, Fe, nickel, Cr, Cu, and Zn — inner at least one sort $0 < x < 1$ — it is — a noble metals element is built into the crystal lattice of B site of the thing which supported at least one sort in the noble-metals element which becomes the perovskite mold multiple oxide shown from Ru, Rh, Pd, Os, Ir, and Pt, or a perovskite mold multiple oxide. The manufacture approach of such a perovskite mold multiple oxide is indicated by the above-mentioned bibliography, and is learned well.

[0010] The catalyst used by this invention can include further Ce and Zr, the heat-resistant oxide with which at least the part serves as a multiple oxide and/or, or the solid solution including rare earth metals other than Ce further, or the heat-resistant oxide which consists of Ce, in order to raise thermal resistance to the component which supported noble metals to the perovskite mold multiple oxide, or was incorporated in the perovskite mold multiple oxide crystal lattice. As for the multiple oxide expressed with a general formula $(\text{CeZrM})\text{O}_2$ (a rare earth metal or alkaline earth metal excluding [M] Ce), as such a heat-resistant oxide, O $(\text{CeSi})_2$, O $(\text{CeZrY})_2$, O $(\text{CeZrLa})_2$, O $(\text{CeZrNd})_2$, O $(\text{CeZrBa})_2$, etc. besides CeO_2 and O $(\text{CeZr})_2$ are desirable. Moreover, since the direction of $\text{CeO}(\text{CeSi})_2$ [O $(\text{CeZr})_2$] is excellent in the effectiveness of maintaining hot clarification activity and O_2 and O $(\text{CeZrBa})_2$ excel two in the effectiveness of maintaining hot clarification activity, further (CeZrY) , it is more desirable.

[0011]

[Function] Drawing 2 (A) and drawing 3 (A) show the catalytic activity after a durability test of the catalyst which supported palladium as noble metals to a perovskite mold multiple oxide. There are not the conventional catalyst 60% window where three components in case the A/F range of fluctuation is ± 0.5 A/F are purified 60% or more is indicated to be to drawing 2 (B) and (C), and a big difference. When the A/F range of fluctuation becomes ± 2.0 A/F, with the catalyst of this invention, 60% window differs from the conventional catalyst the point which is still larger is indicated to be to drawing 3 (B) and (C) notably. Therefore, three components can be purified, even if it performs A/F feedback control and does not stop the A/F range of fluctuation. Moreover, since the A/F range of fluctuation may be large, even if it can install a catalyst directly under [which is easy to receive A/F fluctuation] an engine, and does not keep an exhaust pipe warm on the conditions that exhaust gas temperature, such as the time of engine start up, is low, either or does not heat a catalyst, predetermined gas cleanup effectiveness can be acquired.

[0012]

[Example] Drawing 4 shows the engine with which this invention is applied. The fuel with which the carburetor 20 was formed in the engine 2, and A/F was adjusted is supplied. In the exhaust port of an engine 2, the catalyst 22 is formed in the location [directly under] of an engine 2. Although the oxygen sensor 4 is formed in the upstream of a catalyst 22 by a diagram, an oxygen sensor 4 is for setting up the exhaust gas conditions for a test, and its oxygen sensor 4 is unnecessary as not a thing but the example for carrying out feedback control of A/F with the signal of an oxygen sensor 4. Moreover, although the passage which introduces the compressed air is established in the upstream of a catalyst 22 by a diagram, this is also for setting up the exhaust gas conditions for durability tests, and is unnecessary in the example. The example of this catalyst 22 is shown below. The catalyst in an example and the example of a comparison is supported by heat-resistant honeycomb support, and a diameter is [80mm and the height of the size of the honeycomb support] 95mm — it is cylindrical and the number of cells per two is 400 1cm.

[0013] (Example 1)

[Basic operation A] Slurry coat (support)

The known perovskite mold multiple oxide crystal powder 10 which does not contain noble metals — the 100 weight sections (50 weight sections as an example), The pure-water 150 weight section is added to the known heat-resistant oxide powder 0 — 90 weight sections (50 weight sections as an example). The slurry which carried out grinding mixing for 12 hours and which was obtained with the ball mill is slushed into the honeycomb support of the quality of cordierite. After blowing off and drying the slurry of the complementary section by airstream (it is 24 hours at 130 degrees C), the support which is calcinated among atmospheric air at 600 degrees C for 3 hours and by which coating of a perovskite mold multiple oxide and the heat-resistant oxide was carried out to homogeneity is obtained.

[0014] [Basic operation B] The noble-metals salt water solution which carried out weighing capacity so that it might become the 0.2 — 5.0 weight section by noble-metals conversion to the 100 weight sections of perovskite mold multiple oxide powder and heat-resistant oxide powder among the coating support obtained by the support approach of Pd and the dissolution basic operation A to a perovskite mold multiple oxide crystal is prepared. Coating support is immersed in this water solution or its dilution water solution, and impregnation of the whole quantity of noble metals is carried out to perovskite mold multiple oxide powder and heat-resistant oxide powder, and after desiccation, it calcinates in atmospheric air and considers as the sample for durability tests.

[0015] $(\text{La}_{0.8}\text{Ce}_{0.2})$ The honeycomb inner surface was coated with O3100 weight section by basic operation A at homogeneity $(\text{Fe}_{0.6}\text{Co}_{0.4})$. The amount of coats was 196g per honeycomb volume of 1l. The palladium nitrate water-solution (with product of Tanaka Kikinzoku Kogyo, Inc., it is 4.4 % of the weight by Pd metal) 56.8 weight section which carried out weighing capacity so that it might become the 2.5 weight sections by Pd conversion at this based on basic operation B was melted in the aqua-fortis 100 weight section. pH of this solution was 0.2. After carrying out impregnation of the whole quantity of this solution to the above-mentioned coating honeycomb support, it dried at 130 degrees C for 24 hours, it calcinated at 600 degrees C in atmospheric air for 3 hours, and the sample of an example 1 was obtained.

[0016] (Example 2) The honeycomb inner surface was coated with O350 weight section and O $(\text{Ce}_{0.65}\text{Zr}_{0.30}\text{Y}_{0.05})$ 250 weight section by the basic operation A of an example 1 at homogeneity $(\text{Fe}_{0.6}\text{Co}_{0.4})$. $(\text{La}_{0.8}\text{Ce}_{0.2})$ The amount of coats was 178g per honeycomb volume of 1l. On the other hand, the palladium nitrate water-solution (with product of Tanaka Kikinzoku Kogyo, Inc., it is 4.4 % of the weight by Pd metal) 25 weight section which carried out weighing capacity so that it might become the 1.1 weight section by Pd conversion based on the basic operation B of an example 1 was melted in the aqua-fortis 100 weight section. pH of this solution was

0.2. After carrying out impregnation of the whole quantity of this solution to the above-mentioned coating honeycomb support, it dried at 130 degrees C for 24 hours, it calcinated at 600 degrees C in atmospheric air for 3 hours, and the sample of an example 2 was obtained.

[0017] (Example 3) The honeycomb inner surface was coated with O350 weight section and O(Ce_{0.9}Si_{0.1}) 250 weight section by basic operation A at homogeneity, and the sample of an example 3 was obtained (Fe_{0.56}Co_{0.38}Pd_{0.06}). (La_{0.9}Ce_{0.1}) The amount of coats was 155g per honeycomb volume of 1l. The perovskite mold multiple oxide (La_{0.9}Ce_{0.1}) (Fe_{0.56}Co_{0.38}Pd_{0.06}) O3 of this example incorporates the noble-metals element Pd to the crystal lattice of that B site. An example of the manufacture approach is shown below.

[0018] Metallic elements other than a noble-metals element consider as an alkoxy alcoholate, for example, are prepared as follows.

Lanthanum ethoxy ethylate 36.6g (0.09 mols)

La₃ (OC₂H₄OC₂H₅) Cerium ethoxy ethylate 4.1g (0.01 mols)

Ce₃ (OC₂H₄OC₂H₅) Iron ethoxy ethylate 18.4g (0.056 mols)

Fe₃ (OC₂H₄OC₂H₅) Cobalt ethoxy ethylate 9.0g (0.038 mols)

Co (OC₂H₄OC₂H₅)₂ — these metal alkoxy alcoholates were put into the round bottom flask of 500ml capacity, as an organic solvent, toluene 200ml was added, was agitated and dissolved, and it considered as the mixed alkoxy alcoholate solution.

[0019] On the other hand, the noble-metals element was prepared as a water-soluble salt, and the water solution which added 100ml of deionized water to 12.1g (Pd part 4.4wt(s)%) (equivalent to 0.53g and 0.006 mols at Pd conversion) of palladium nitrate solutions as the water solution was prepared. It was gradually dropped under the room temperature into the previous mixed alkoxy alcoholate solution, having palladium nitrate poured [this] it for about 15 minutes. Brown precipitation generates promptly by dropping of a palladium nitrate water solution, and it becomes viscosity gradually. After agitating the solution under a room temperature for 2 hours, moisture and the toluene of an organic solvent were distilled off out of the system of reaction under reduced pressure, and the precursor of a dark-brown LaCeFeCoPd oxide was obtained.

[0020] After moving the viscous object of this precursor to the petri dish and carrying out draught drying at 60 degrees C for 24 hours, among air, it heat-treated at 600 degrees C with the electric furnace for 2 hours, and dark-brown powder was obtained. The powder was the perovskite mold single crystal phase of O(Fe(La_{0.9}Ce_{0.1})_{0.56}Co_{0.38}Pd_{0.06}) 3 from the result of a powder X diffraction.

[0021] (Example 4) The honeycomb inner surface was coated with O350 weight section and O(Ce_{0.8}Zr_{0.15}Ba_{0.05}) 250 weight section by basic operation A at homogeneity, and the sample of an example 4 was obtained (Co_{0.9}Pd_{0.06}Pt_{0.04}). (La_{0.8}Sr_{0.2}) The amount of coats was 161g per honeycomb volume of 1l. The perovskite mold multiple oxide (La_{0.8}Sr_{0.2}) (Co_{0.9}Pd_{0.06}Pt_{0.04}) O3 of this example incorporates the noble-metals elements Pd and Pt to the crystal lattice of that B site, and that manufacture approach of it is the same as that of an example 3.

[0022] (Example 5) The honeycomb inner surface was coated with O380 weight section and O(Zr_{0.8}Ce_{0.2}) 220 weight section by basic operation A at homogeneity, and the sample of an example 5 was obtained (Mn_{0.5}Co_{0.4}Pd_{0.05}Ru_{0.05}). (La_{0.2}Ba_{0.8}) The amount of coats was 172g per honeycomb volume of 1l. The perovskite mold multiple oxide (La_{0.2}Ba_{0.8}) (Mn_{0.5}Co_{0.4}Pd_{0.05}Ru_{0.05}) O3 of this example incorporates the noble-metals elements Pd and Ru to the crystal lattice of that B site, and that manufacture approach of it is the same as that of an example 3.

[0023] ((a) The example of a comparison) The catalyst which made the heat-resistant oxide powder (Ce_{0.8}Zr_{0.2}) O2 live together was used for Pt-Rh/gamma-aluminum 2O3 which is the conventional catalyst for automobiles. The weight ratio of gamma-aluminum 2O3, and O (Ce_{0.8}Zr_{0.2})₂, Pt and Rh was 50:50:0.4:0.12. The amount of coats was 208g per honeycomb volume of 1l.

[0024] ((b) The example of a comparison) The catalyst which made the heat-resistant oxide powder (Ce_{0.8}Zr_{0.2}) O2 live together was used for Pd/gamma-aluminum 2O3 which is the conventional catalyst for automobiles. The weight ratio of gamma-aluminum 2O3, and O (Ce_{0.8}Zr_{0.2})₂ and Pd was 50:50:2.5. The amount of coats was 212g per honeycomb volume of 1l.

[0025] (Durability test conditions) With the carburetor specification engine shown in drawing 4, each catalyst of an example and the example of a comparison was attached in the flue system whose displacement is 0.66l., it adjusted so that the interior temperature of a catalyst might become 950 degrees C, and the durability test was performed for 50 hours. By adjusting so that it may be set to A/F=13.5, and introducing the compressed air into the lower stream of a river of an engine 2, the fuel flow of the carburetor 20 under the durability test was set up so that the exhaust gas included in a catalyst 22 might serve as theoretical air fuel ratio (A/F=14.6).

[0026] (Assessment of the catalytic activity after a durability test) Each catalyst of an example and the example of a comparison was attached in the flue system of the same carburetor specification engine as a durability test. The fuel flow of a carburetor 20 was adjusted so that it might be set to A/F=13.5, it attached the heat exchanger in the lower stream of a river of an engine 2, and it set it up so that the exhaust gas temperature included in a catalyst 22 might become 400 degrees C. When fluctuation of A/F was measured with the oxygen sensor 4 attached just before the catalyst 22, it was 1.5Hz in frequency in amplitude**2.0 A/F. Moreover, the capacity which passes a catalyst 22 was about 70000-/o'clock in space velocity (SV). The gas before and behind a catalyst is measured with an automobile exhaust analyzer, and the result of having asked for the rate of clarification by each catalyst is shown in a table 1.

[0027]

[A table 1]

	ペロブスカイト型複合酸化物	耐熱酸化物	追加 貴金属	コート量 (g/l)	浄化率(%)		
					CO	THC	NOx
実施例							
1	[100] (La _{0.8} Ce _{0.2}) (Fe _{0.6} Co _{0.4})O ₃	—	(2.5) Pd	196	68	87	86
2	[50] (La _{0.8} Ce _{0.2}) (Fe _{0.6} Co _{0.4})O ₃	[50] (Ce _{0.65} Zr _{0.35} Y _{0.05})O ₂	(1.1) Pd	178	63	89	81
3	[50] (La _{0.9} Ce _{0.1}) (Fe _{0.56} Co _{0.38} Pd _{0.06})O ₃	[50] (Ce _{0.8} Si _{0.1})O ₂	—	155	71	94	84
4	[50] (La _{0.8} Si _{0.2}) (Co _{0.9} Pd _{0.06} Pt _{0.04})O ₃	[50] (Ce _{0.8} Zr _{0.15} Ba _{0.05})O ₂	—	161	67	84	82
5	[80] (La _{0.2} Ba _{0.8}) (Mn _{0.5} Co _{0.4} Pd _{0.05} Ru _{0.05})O ₃	[20] (Zr _{0.8} Ce _{0.2})O ₂	—	172	74	75	77
比較例							
a	—	[50] γ -Al ₂ O ₃	(0.4) Pt	208	4	22	78
b	—	[50] (Ce _{0.8} Zr _{0.2})O ₂	(0.12) Rh				
		[50] γ -Al ₂ O ₃	(2.5) Pd	212	0	29	41
		[50] (Ce _{0.8} Zr _{0.2})O ₂					

(備考) [] 内の数値は重量部を表わす。

コート量は焼成後のハニカム容積 1 リットル当りの g 数である。

浄化率(%)は A/F = 13.5 での測定値である。

[0028] With the flue system which does not perform A/F feedback control like a carburetor specification engine from the result of a table 1, as a result of the A/F range's of fluctuation becoming large, in the examples a and b of a comparison using the catalyst which supported the noble-metals element to the alumina, catalytic activity is low and cannot present practical use. In the example using the catalyst which supported the noble-metals element to the perovskite mold multiple oxide, or was incorporated to the crystal lattice, it turns out to it that an average of A/F is purifying three components of CO, THC, and NOx 60% or more in the range larger than 13-15, and can present practical use.

[0029]

[Effect of the Invention] Since three components of CO, THC, and NOx can be purified even if it does not perform A/F feedback control in this invention, an oxygen sensor and expensive components, such as ECU and EFI, cannot be needed, but cost can be lowered. Moreover, since a catalyst can be arranged directly under an engine, in order to keep a catalyst warm, an exhaust pipe is used as a double pipe, or a cure, such as forming a heater, also becomes unnecessary, and it comes out to aim at cost lowering also at this

point.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram showing the conventional exhaust gas purge.

[Drawing 2] It is drawing showing the clarification property of various catalysts in case A/F fluctuation is **0.5 A/F.

[Drawing 3] It is drawing showing the clarification property of various catalysts in case A/F fluctuation is **2.0 A/F.

[Drawing 4] It is the outline block diagram showing one example.

[Description of Notations]

2 Engine

4 Oxygen Sensor

20 Carburetor

22 Catalyst

[Translation done.]

1

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(71) 出願人 000002967

ダイハツ工業株式会社

大阪府池田市ダイハツ町1番1号

(72) 発明者 田中 裕久

滋賀県蒲生郡竜王町大字山之上3000番地

ダイハツ工業株式会社滋賀テクニカルセン
ター内

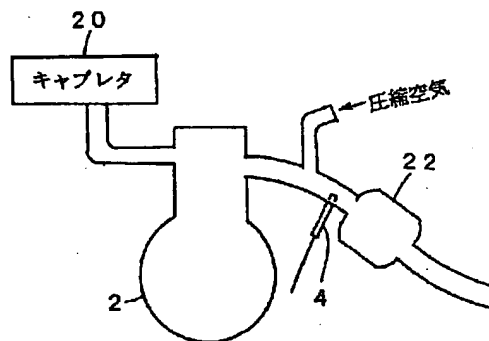
(74) 代理人 弁理士 野口 繁雄

(54) 【発明の名称】 自動車排ガス浄化装置

(57) 【要約】

【目的】 A/Fフィードバック制御を行なわなくても排ガスの3成分を浄化できるようにする。

【構成】 エンジン2にはキャブレタ20が設けられてA/Fが調整された燃料が供給される。エンジン2の排気口にはエンジン2の直下の位置に触媒22が設けられている。酸素センサの信号によるA/Fのフィードバック制御は行なわない。触媒22として、Pdなどの貴金属をペロブスカイト型複合酸化物に担持し又はペロブスカイト型複合酸化物結晶格子中に取り込んだ触媒を用いる。



【特許請求の範囲】

【請求項1】 キャブレタや簡易型燃料噴射装置を備えたエンジンであって、エンジン排気口の酸素センサの信号による空燃比フィードバック制御を行わないエンジンに用いる排ガス浄化装置であり、エンジンの排気口に、排ガス浄化用触媒として、貴金属をペロブスカイト型複合酸化物に担持し又はペロブスカイト型複合酸化物結晶格子中に取り込んだ触媒を設けたことを特徴とする自動車排ガス浄化装置。

【請求項2】 触媒が設けられている位置は、エンジン直下である請求項1に記載の自動車排ガス浄化装置。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は一酸化炭素(CO)、炭化水素(THC)及び酸化窒素(NOx)の浄化能力に優れた自動車排ガス浄化装置に関するものである。

【0002】

【従来の技術】 排ガス浄化用三元触媒としてはアルミナ担体にPt、Rh、Pdなどの貴金属を担持した貴金属触媒が実用化されて広く使用されている。自動車排ガス浄化装置は、図1に示されるように、エンジン2の排気口に酸素センサ4を設けて排ガスの酸素濃度を検出し、その検出信号を基にしてコンピュータ(ECU)6でA/F(空燃比)を演算し、A/Fが所定の範囲に入るように、エンジン2に燃料を噴射する電子式燃料噴射装置(EFI)8を制御している。

【0003】 図2と図3に、サンプルを理論空燃比(A/F=14.6)に設定されたエンジン排ガス中、950℃で60時間の耐久試験を行なった後、そのサンプルをテストピースサイズ(直径30mm、高さが25mmの円筒状)にくり抜き、モデルガス試験機にてSV(空間速度)=70000/時の条件にて測定した各種触媒の活性を示す。(A)～(C)の各図の左側の図は理論空燃比での温度に対する浄化率を示しており、右側の図は触媒に入るガス温度を400℃に設定して測定したときのA/Fに対する浄化率を示している。それぞれの図の(A)は後で説明する一実施例であるペロブスカイト型複合酸化物にPdを担持した触媒(実施例3)、

(B)はアルミナにPdを担持した従来の触媒(比較例b)、(C)はアルミナにPtとRhを担持した従来の触媒(比較例a)と同仕様に調整したものである。

【0004】 図2は各A/Fでの変動が±0.5 A/Fの場合であり、CO、THC及びNOxのそれぞれの浄化率が60%以上を確保できるA/Fの範囲(60%ウインド)が(B)、(C)の従来の触媒にも存在する。一方、図3は各A/Fでの変動が±2.0 A/Fの場合であり、(B)及び(C)に示されるように、知従来の触媒では各A/Fでの変動が±2.0 A/Fにも大きくなると、COの浄化率が低下し、3成分を同時に60%以上浄化できる60%ウインドがなくなってしまう。そ

のため、従来の浄化装置は、図1に示されるようなA/Fフィードバック制御を行なうことによって、A/Fの変動が±0.5を越えず、かつA/Fが図2(B)、(C)で示される60%ウインド内にくるようにしている。

【0005】 また、エンジンからの排ガスはエンジン直下ではエンジンのサイクルによりA/Fが大きく変動する。そのため、従来のように触媒の位置でのA/F変動を抑えるためには、エンジン気筒毎のA/F変動を緩和できるように触媒はエンジンから遠く離れた位置に設置しなければならず、一般に床下と呼ばれる車両ボディ下部に取付けられている。一方、排ガス温度が低下すると触媒活性は低下する。例えば、各A/Fでの変動が±0.5 A/Fの場合には200℃以下では殆ど触媒活性がなくなり、各A/Fでの変動が±2.0 A/Fにも大きくなると、図3(B)、(C)の左側の図からわかるように、従来の触媒では350～400℃以下ですでに触媒活性を示さなくなる。触媒をエンジンから遠く離れた位置に設置すると、エンジンからの排ガスが触媒に到達するまでに冷えるため、エンジン始動時など排ガス温度が低い条件では触媒が不活性となり、排ガスが浄化されない問題が生じる。そのため、エンジンから触媒までの排気管を二重管にして保温する等の対策も講じられている。

【0006】 触媒としては、希土類金属、アルカリ土類金属及び遷移金属から構成されるペロブスカイト型複合酸化物に貴金属を共存させた触媒は、CO、HC及びNOxを浄化する安価な排ガス浄化用三元触媒として実用化が期待されている(特開昭59-87046号公報、特開昭60-82138号公報、特開平1-168343号公報参照)。この触媒はアルミナに貴金属を担持させた従来の触媒の代りに使用されるものであり、この触媒を使用する排ガス浄化装置も図1に示されるようなA/Fフィードバック制御を備えた排ガス浄化装置が予定されている。

【0007】

【発明が解決しようとする課題】 図1に示されるようなA/Fフィードバック制御を行なうと、酸素センサ、ECU、EFIといった高価な部品を必要とし、それだけコスト高になる。また、触媒をエンジンから遠く離れた位置に設置すると、エンジンからの排ガスが触媒に到達するまでに冷えるため、特にエンジン始動時にも触媒を機能させるためには、エンジンから触媒までの排気管を二重管にして保温するようになり、それでも十分でない場合は触媒を加熱するなどの対策も必要になる。本発明は酸素センサ、ECU、EFIといった高価な部品を用いてA/Fフィードバック制御を行なわなくても、キャブレタ(化器)や簡易型燃料噴射装置を用いるだけでも排ガスが浄化される浄化装置を提供することを目的とするものである。

【0008】

【課題を解決するための手段】本発明の排ガス浄化装置は、エンジン排気口の酸素センサの信号による空燃比フィードバック制御を行なわないエンジンに適用するものである。そして、排ガス浄化用触媒として、貴金属をペロブスカイト型複合酸化物に担持し又はペロブスカイト型複合酸化物結晶格子中に取り込んだ触媒を用いる。触媒が設けられている位置をエンジン直下とすれば、排ガスが冷却されるのが抑えられるので、排ガスを保温する手段や触媒を加熱する手段が不要になり、冷間にてエンジンを始動した直後から触媒が働き、排ガス浄化にとって有利である。

【0009】本発明で使用する触媒は、 $(A_{1-x}A'_x)BO_3$ 、(式中、AはLa、Nd及びPrのうちの少なくとも1種、A'はCe、Mg、Ca、Sr、Ba及びYのうちの少なくとも1種、BはCo、Mn、Fe、Ni、Cr、Cu及びZnのうちの少なくとも1種、 $0 < x < 1$ である)で示されるペロブスカイト型複合酸化物に、Ru、Rh、Pd、Os、Ir及びPtからなる貴金属元素のうちの少なくとも1種を担持したもの、又は

20 【実施例】図4は本発明が適用されるエンジンを示したものである。エンジン2にはキャブレタ20が設けられてA/Fが調整された燃料が供給される。エンジン2の排気口にはエンジン2の直下の位置に触媒22が設けられている。図では酸素センサ4が触媒22の上流に設けられているが、酸素センサ4はテスト用の排ガス条件を設定するためのものであり、酸素センサ4の信号によってA/Fをフィードバック制御するためのものではなく、実施例としては酸素センサ4は不要である。また、図では触媒22の上流に圧縮空気を導入する流路が設けられているが、これも耐久試験用の排ガス条件を設定するためのものであり、実施例では不要である。この触媒22の例を以下に示す。実施例及び比較例における触媒は、耐熱性ハニカム担体に担持されたものであり、そのハニカム担体のサイズは、直径が80mm、高さが95mmの円筒状であり、 1cm^2 当りのセル数は400である。

【0010】(実施例1)

【基本操作A】スラリーコート(担持)

30 貴金属を含んでいない既知のペロブスカイト型複合酸化物結晶粉末10~100重量部(一例として50重量部)と、既知の耐熱性酸化物粉末0~90重量部(一例として50重量部)に純水150重量部を加え、ボールミルで12時間粉碎混合して得たスラリーをコーゼライト質のハニカム担体に流し込み、余部のスラリーを空気流で吹き払い、乾燥(例えば130℃で24時間)させた後、600℃で大気中3時間焼成してペロブスカイト型複合酸化物と耐熱性酸化物が均一にコーティングされた担体を得る。

【0010】本発明で使用する触媒は、貴金属をペロブスカイト型複合酸化物に担持し又はペロブスカイト型複合酸化物結晶格子中に取り込んだ成分に、耐熱性を高めるために、Ce及びZr、又はさらにCe以外の希土類金属を含み少なくとも一部が複合酸化物及び/もしくは固溶体となっている耐熱性酸化物、又はCeからなる耐熱性酸化物をさらに含ませることができる。そのような耐熱性酸化物としては、 CeO_2 、 $(CeZr)O_2$ の他、 $(CeSi)O_2$ 、 $(CeZrY)O_2$ 、 $(CeZrLa)O_2$ 、 $(CeZrNd)O_2$ 、 $(CeZrBa)O_2$ など、一般式 $(CeZrM)O_2$ (MはCeを除く希土類金属又はアルカリ土類金属)で表わされる複合酸化物が好ましい。また、 CeO_2 よりは $(CeZr)O_2$ や $(CeSi)O_2$ の方が高温における浄化活性を維持する効果に優れ、更に $(CeZrY)O_2$ や $(CeZrBa)O_2$ の方が高温における浄化活性を維持する効果に優れているのでより好ましい。

【0011】

【作用】図2(A)と図3(A)は、ペロブスカイト型複合酸化物に貴金属としてパラジウムを担持した触媒の、耐久試験後の触媒活性を示したものである。A/F変動幅が ± 0.5 A/Fである場合の3成分が60%以上浄化される60%ウインドは、図2(B)、(C)に示される従来の触媒と大きな相違はない。A/F変動幅が ± 2.0 A/Fになると、本発明の触媒では60%ウインドは更に広がっている点が図3(B)、(C)に

40 【0014】【基本操作B】Pdの担持方法及びペロブスカイト型複合酸化物結晶への固溶
基本操作Aで得たコーティング担体のうち、ペロブスカイト型複合酸化物粉末と耐熱性酸化物粉末の100重量部に対して、貴金属換算で0.2~5.0重量部となるように秤量した貴金属塩水溶液を用意する。この水溶液又はその希釈水溶液にコーティング担体を浸漬して貴金属の全量をペロブスカイト型複合酸化物粉末と耐熱性酸化物粉末に含浸させ、乾燥後、大気中で焼成して耐久試験用サンプルとする。

50 【0015】 $(La_{0.2}Ce_{0.8})(Fe_{0.2}Co_{0.8})O_{1.0}$ 00重量部を基本操作Aによりハニカム内面に均一にコ

ーティングした。コート量はハニカム容積1リットル当たり196gであった。これに基本操作Bに基づきPd換算で2.5重量部となるように秤量した硝酸パラジウム水溶液(田中貴金属工業株式会社の製品で、Pd金属分4.4重量%)56.8重量部を希硝酸100重量部に溶かした。この溶液のpHは0.2であった。この溶液の全量を上記のコーティングハニカム担体中含浸させた後、130℃で24時間乾燥し、大気中で600℃で3時間焼成して実施例1のサンプルを得た。

【0016】(実施例2) $(La_{0.5}Ce_{0.5})(Fe_{0.5}Co_{0.5})O_{5.0}$ 重量部と $(Ce_{0.5}Zr_{0.5}Y_{0.5})O_{2.5}$ 重量部を実施例1の基本操作Aによりハニカム内面に均一にコーティングした。コート量はハニカム容積1リットル当たり178gであった。これに対し、実施例1の基本操作Bに基づきPd換算で1.1重量部となるように秤量した硝酸パラジウム水溶液(田中貴金属工業株式会社の製品で、Pd金属分4.4重量%)25重量部を*

ランタンエトキシエチレート
 $La(OC_2H_4OC_2H_5)_3$
 セリウムエトキシエチレート
 $Ce(OC_2H_4OC_2H_5)_3$
 鉄エトキシエチレート
 $Fe(OC_2H_4OC_2H_5)_3$
 コバルトエトキシエチレート
 $Co(OC_2H_4OC_2H_5)_3$

これらの金属アルコキシアルコラートを500ml容量の丸底フラスコに入れ、有機溶媒としてトルエン200mlを加えて攪拌し、溶解させて混合アルコキシアルコラート溶液とした。

【0019】一方、貴金属元素は水溶性の塩として用意し、その水溶液として硝酸パラジウム溶液(Pd分4.4wt%)12.1g(Pd換算で0.53g、0.006モルに相当)に脱イオン水100mlを加えた水溶液を調製した。この硝酸パラジウム水溶液を先の混合アルコキシアルコラート溶液中に室温下で約15分間かけて徐々に滴下した。硝酸パラジウム水溶液の滴下により直ちに褐色の沈澱が生成し、次第に粘稠となる。その溶液を室温下で2時間攪拌した後、減圧下で水分と有機溶媒のトルエンとを反応系外に留去し、黒褐色の $LaCeFeCoPd$ 酸化物の前駆体を得た。

【0020】この前駆体の粘稠物をシャーレに移し、60℃で24時間通風乾燥した後、空气中、電気炉で600℃で2時間熱処理して黒褐色の粉末を得た。その粉末は粉末X線回折の結果から、 $(La_{0.5}Ce_{0.5})(Fe_{0.5}Co_{0.5}Pd_{0.5})O_5$ のペロブスカイト型単一結晶相であった。

【0021】(実施例4) $(La_{0.5}Sr_{0.5})(Co_{0.5}Pd_{0.5}Pt_{0.5})O_{5.0}$ 重量部と $(Ce_{0.5}Zr_{0.5}Ba_{0.5})O_{2.5}$ 重量部を基本操作Aによりハニカム内面に均一にコーティングして実施例4のサンプルを得た。コ

*希硝酸100重量部に溶かした。この溶液のpHは0.2であった。この溶液の全量を上記のコーティングハニカム担体中含浸させた後、130℃で24時間乾燥し、大気中で600℃で3時間焼成して実施例2のサンプルを得た。

【0017】(実施例3) $(La_{0.5}Ce_{0.5})(Fe_{0.5}Co_{0.5}Pd_{0.5})O_{5.0}$ 重量部と $(Ce_{0.5}Si_{0.5})O_{2.5}$ 重量部を基本操作Aによりハニカム内面に均一にコーティングして実施例3のサンプルを得た。コート量はハニカム容積1リットル当たり155gであった。この実施例のペロブスカイト型複合酸化物 $(La_{0.5}Ce_{0.5})(Fe_{0.5}Co_{0.5}Pd_{0.5})O_5$ は、そのBサイトの結晶格子に貴金属元素Pdを取り込んだものである。その製造方法の一例を次に示す。

【0018】貴金属元素以外の金属元素はアルコキシアルコラートとして、例えば以下のように用意する。

36.6g (0.09モル)

4.1g (0.01モル)

18.4g (0.056モル)

9.0g (0.038モル)

ート量はハニカム容積1リットル当たり161gであった。この実施例のペロブスカイト型複合酸化物 $(La_{0.5}Sr_{0.5})(Co_{0.5}Pd_{0.5}Pt_{0.5})O_5$ は、そのBサイトの結晶格子に貴金属元素PdとPtを取り込んだものであり、その製造方法は実施例3と同様である。

【0022】(実施例5) $(La_{0.5}Ba_{0.5})(Mn_{0.5}Co_{0.5}Pd_{0.5}Ru_{0.5})O_{8.0}$ 重量部と $(Zr_{0.5}Ce_{0.5})O_{2.0}$ 重量部を基本操作Aによりハニカム内面に均一にコーティングして実施例5のサンプルを得た。コート量はハニカム容積1リットル当たり172gであった。この実施例のペロブスカイト型複合酸化物 $(La_{0.5}Ba_{0.5})(Mn_{0.5}Co_{0.5}Pd_{0.5}Ru_{0.5})O_8$ は、そのBサイトの結晶格子に貴金属元素PdとRuを取り込んだものであり、その製造方法は実施例3と同様である。

【0023】(比較例a)従来の自動車用触媒であるPt-Rh/ $\gamma-Al_2O_3$ に耐熱性酸化物粉末 $(Ce_{0.5}Zr_{0.5})O_2$ を共存させた触媒を使用した。 $\gamma-Al_2O_3$ 、 $(Ce_{0.5}Zr_{0.5})O_2$ 、Pt及びRhの重量比は50:50:0.4:0.12であった。コート量はハニカム容積1リットル当たり208gであった。

【0024】(比較例b)従来の自動車用触媒であるPd/ $\gamma-Al_2O_3$ に耐熱性酸化物粉末 $(Ce_{0.5}Zr_{0.5})O_2$ を共存させた触媒を使用した。 $\gamma-Al_2O_3$ 、 $(Ce_{0.5}Zr_{0.5})O_2$ 及びPdの重量比は50:

50:2.5であった。コート量はハニカム容積1リットル当たり212gであった。

【0025】（耐久試験条件）図4に示されたキャブレタ仕様エンジンで、排気量が0.66リットルの排気システムに実施例、比較例のそれぞれの触媒を取りつけ、触媒内部温度が950℃になるように調整し、50時間耐久試験を行なった。その耐久試験中のキャブレタ20の燃料流量は $A/F = 13.5$ となるように調整し、エンジン2の下流には圧縮空気を導入することにより、触媒22に入る排ガスが理論空燃比（ $A/F = 14.6$ ）となるように設定した。

【0026】（耐久試験後の触媒活性の評価）耐久試験と同じキャブレタ仕様エンジンの排気システムに実施

例、比較例のそれぞれの触媒を取りつけた。キャブレタ20の燃料流量は $A/F = 13.5$ となるように調整し、エンジン2の下流に熱交換器を取りつけ、触媒22に入る排ガス温度が400℃となるように設定した。触媒22の直前に取りつけた酸素センサ4で A/F の変動を測定したところ、振幅±2.0 A/F で、周波数1.5Hzであった。また、触媒22を通過するガス量は空間速度（SV）で約70000/時であった。触媒前後のガスを自動車排ガス分析計にて測定し、各触媒による浄化率を求めた結果を表1に示す。

【0027】

【表1】

	ペロブスカイト型複合酸化物	耐熱酸化物	追加 貴金属	コート量 (g/l)	浄化率(%)		
					CO	THC	NOx
実施例							
1	[100] (La _{0.8} Ce _{0.2}) (Fe _{0.6} Co _{0.4})O ₃	—	(2.5) Pd	1.96	68	87	86
2	[50] (La _{0.8} Ce _{0.2}) (Fe _{0.5} Co _{0.4})O ₃	[50] (Ce _{0.85} Zr _{0.30} Y _{0.05})O ₂	(1.1) Pd	1.78	63	89	81
3	[50] (La _{0.8} Ce _{0.1}) (Fe _{0.55} Co _{0.35} Pd _{0.05})O ₃	[50] (Ce _{0.8} Si _{0.1})O ₂	—	1.55	71	94	84
4	[50] (La _{0.8} Si _{0.2}) (Co _{0.8} Pd _{0.05} Pt _{0.04})O ₃	[50] (Ce _{0.8} Zr _{0.15} Ba _{0.05})O ₂	—	1.61	67	84	82
5	[80] (La _{0.2} Ba _{0.8}) (Mn _{0.5} Co _{0.4} Pd _{0.05} Ru _{0.05})O ₃	[20] (Zr _{0.8} Ce _{0.2})O ₂	—	1.72	74	75	77
比較例							
a	—	[50] γ-Al ₂ O ₃ [50] (Ce _{0.8} Zr _{0.2})O ₂	[0.4] Pt [0.12] Rh	2.08	4	22	78
b	—	[50] γ-Al ₂ O ₃ [50] (Ce _{0.8} Zr _{0.2})O ₂	[2.5] Pd	2.12	0	29	41

(備考) [] 内の数値は重量部を表わす。

コート量は焼成後のハニカム容積1リットル当りのg数である。

浄化率(%)はA/F=13.5での測定値である。

【0028】表1の結果から、キャブレタ仕様エンジンのようにA/Fフィードバック制御を行わない排気システムでは、A/F変動幅が大きくなる結果、アルミナに貴金属元素を担持した触媒を用いる比較例a、bでは触媒活性が低く、実用に供することができない。それに対し、ペロブスカイト型複合酸化物に貴金属元素を担持し、またはその結晶格子に取り込んだ触媒を用いた実施例では平均A/Fが13~15よりも広い範囲でCO、THC及びNOxの3成分を60%以上浄化しており、実用に供しうることがわかる。

【0029】

【発明の効果】本発明ではA/Fフィードバック制御を行わなくてもCO、THC及びNOxの3成分を浄化することができるので、酸素センサ、ECU、EFIといった高価な部品を必要とせず、コストを下げることができる。また、触媒をエンジン直下に配置することができるので、触媒を保温するために排気管を二重管にしたり、ヒータを設けるなどの対策も不要になり、この点でもコスト低下を図ることができる。

【図 1】従来の排ガス浄化装置を示す概略図である。

【図 2】A/F変動が ± 0.5 A/Fである場合の各種触媒の浄化特性を示す図である。

【図 3】A/F変動が ± 2.0 A/Fである場合の各種触媒の浄化特性を示す図である。

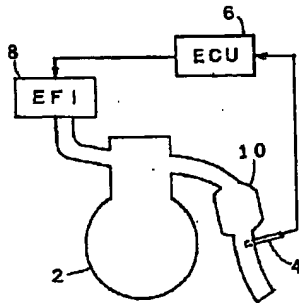
【図 4】一実施例を示す概略構成図である。

*

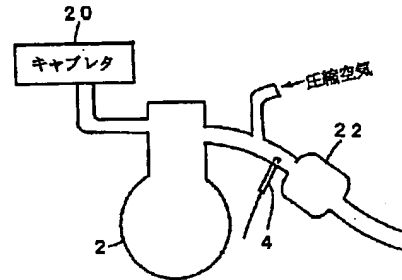
*【符号の説明】

2 エンジン
4 酸素センサ
20 キャブレタ
22 触媒

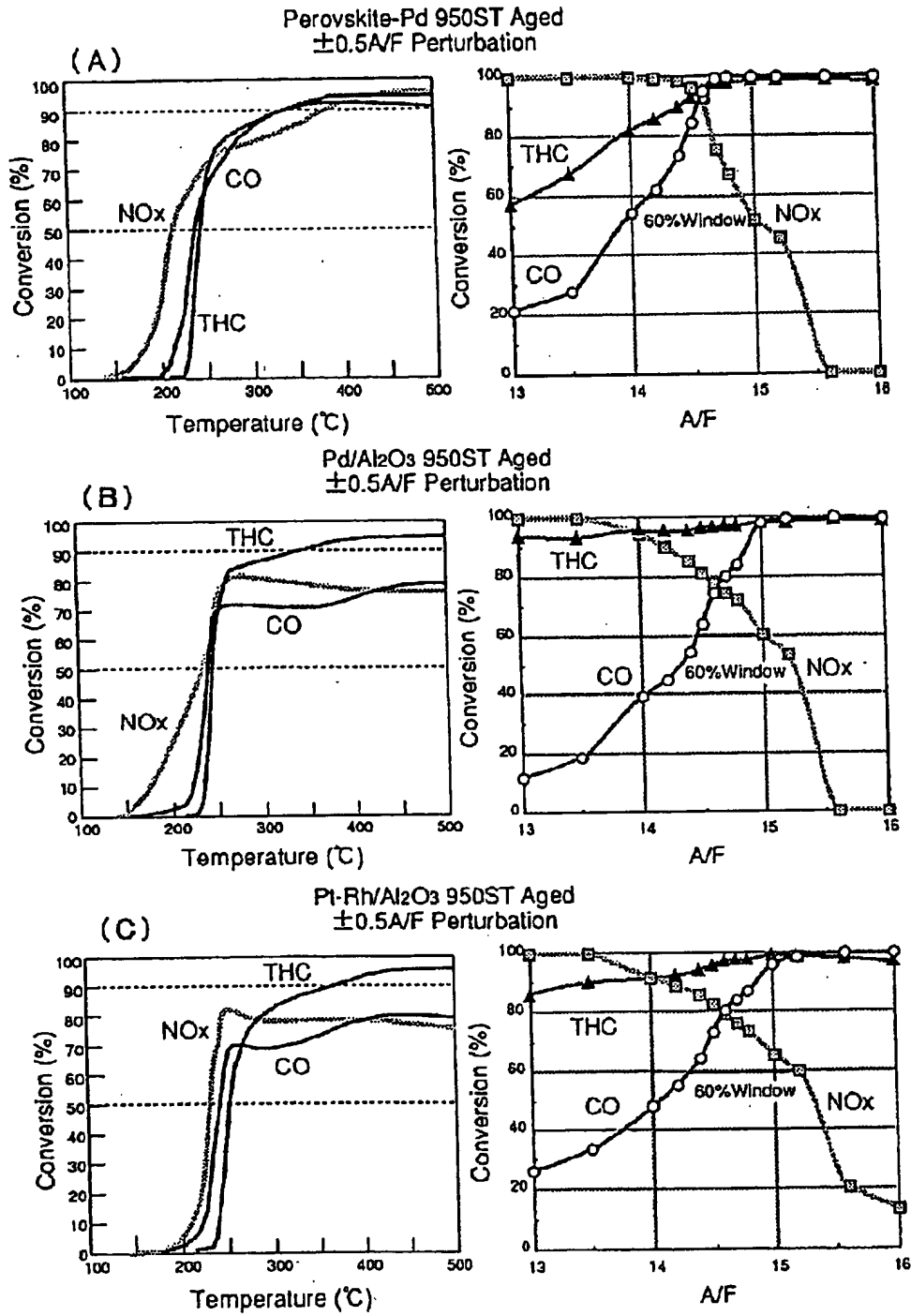
【図 1】



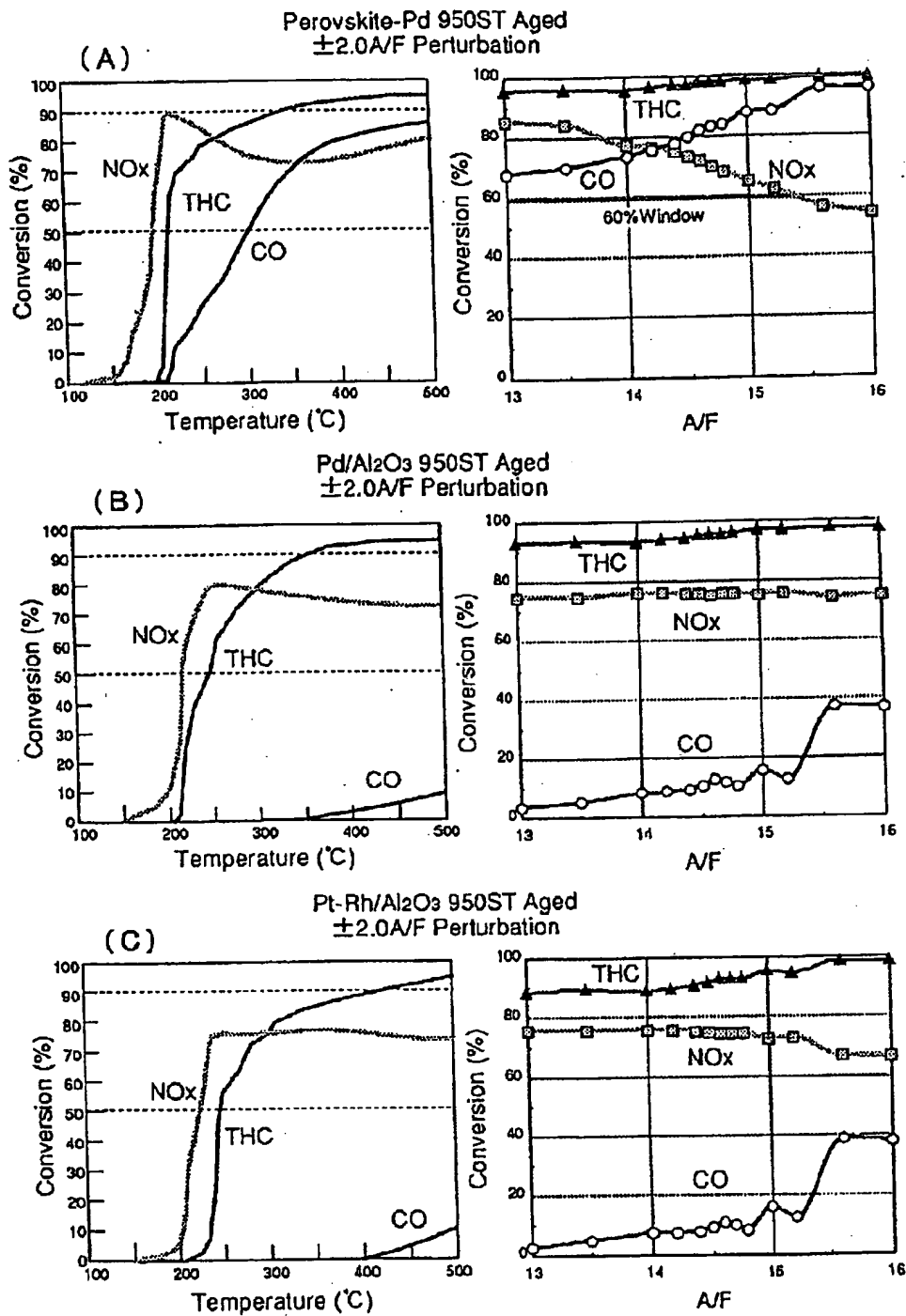
【図 4】



【図2】

Catalytic Activity under $\pm 0.5A/F$ Perturbation

【図3】

Catalytic Activity under $\pm 2.0A/F$ Perturbation

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